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SEMICONDUCTOR GRADE, SOLAR SILICON PURIFICATION PROJECT

Motorola Report No. 2257/8

Technical Quarterly Report No. 8

JPL CONTRACT NO. 954442

By

William M. Ingle

Principal Investigator

Robert Chaney, Stephen Thompson, Dick Rosler, and John Jackson

Period Covered: 1 October 1977 - 31 December 1977

Date Issued: 21 December 1977

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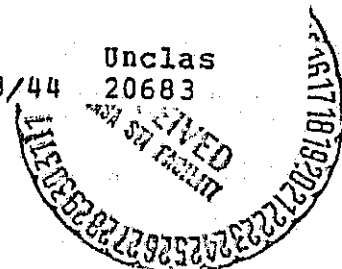
This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Department of Energy, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

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ABSTRACT

The technical progress reported in the current quarterly report can be divided into five task areas. They are as follows:

Spectroscopic Analysis and Characterization of the $(\text{SiF}_2)_x$ Polymer and Si_xF_y Homologues. Preliminary analysis utilizing N.M.R., T.G.A., D.S.C. and Mass Spec. are consistent with both the $(\text{SiF}_2)_x$ polymer and Si_xF_y homologues being nearly identical in chemical composition (mainly SiF_2 group in long chain polymers or cyclic homologues) and thermal stability.

Experiments Involving Si_xF_y Homologue Conversion Chemical Vapor Deposition of Silicon. Results from these experiments demonstrate that a bed of heated (850°C) silicon chunks is an effective way to convert the homologues into silicon in high yield.

Demonstration Runs on the Near-Continuous Apparatus. The near-continuous apparatus has been operated at rates >25 gm/hr in two multi-hour series of runs for silicon production and parameter optimization. In the most recent series, the apparatus was operated for 8 hours in a near-continuous fashion during which 155 grams of silicon was purified and a weighed silicon mass balance revealed $\sim 100\%$ of the silicon accounted for.

Economic Analysis. An economic analysis incorporating a Si_xF_y recycle step in the purification process reduces the cost of purifying silicon via the present process (assuming, \$10MM fixed capital investment) to \$7.68/Kg Si.

Silicon Sample Analysis. Representative silicon samples have been submitted for SSMS elemental analyses. As they become available they will be reported.

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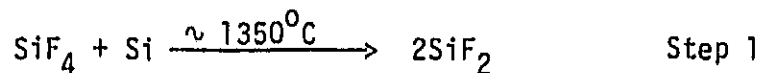
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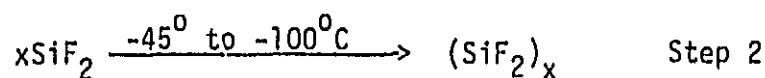
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I INTRODUCTION

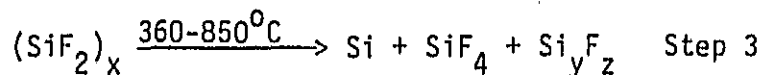
The purpose of the present investigation is to convert metallurgical grade silicon (mg Si) into semiconductor grade silicon (sg Si) via a 3 step SiF_2 polymer transport purification process. The first step¹ involves the reaction of SiF_4 with mg Si to yield gaseous SiF_2 :



This is followed by a polymer formation step.²



The polymer is then converted into high purity silicon, SiF_4 and higher homologues.³



The mg Si undergoes purification in all three steps of the above transport processes.

Progress is reported on the project in four major areas. These are:

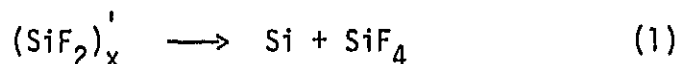
- i) Spectroscopic analysis and characterization of the $(\text{SiF}_2)_x$ polymer and Si_xF_y homologues.
- ii) Experiments involving Si_xF_y homologue conversion.
- iii) Demonstration Runs on the near-continuous apparatus.
- iv) Economic Analysis
- v) Elemental Analysis.

Finally, conclusions on current results will be presented in conjunction with recommendations for future work.

II EXPERIMENTAL

A. Polymer Conversion

A series of experiments has been undertaken to investigate the conversion of unconverted polymer residue into product.



The studies on homologue conversion into silicon and SiF_4 have been directed toward optimizing conditions for conversion of Si_xF_y homologues generated from $(\text{SiF}_2)_x$ polymer at temperatures greater than 160°C . In earlier experiments thermal disproportionation of the homologues with conversion efficiencies of 78% had been demonstrated on a 2 inch quartz reactor at temperatures up to 850°C , using the batch method for polymer formation.⁴ Quartz was chosen as the preferred substrate for initial thermal disproportionation studies due to the ease of construction, modification, and cleaning of a quartz reactor as opposed to more conventional substrates such as silicon, tungsten or molybdenum. A batch method of polymer formation and conversion was chosen due to the greater capability of obtaining quantitative results as opposed to a semi-continuous method of deposition and conversion. It will be noted, however, that data obtained using the batch method of polymer conversion is directly applicable to a semi-continuous mode of polymer formation and conversion.

An apparatus has been designed utilizing the basic concepts of the condensation-disproportionation coil, while incorporating a high temperature zone for the residual polymer $(\text{SiF}_2)_x$ disproportionation reaction. In this apparatus the volatile products of the oils generated at low temperatures $<400^\circ\text{C}$ are passed across a high temperature ($750^\circ\text{C} - 950^\circ\text{C}$) quartz hot zone where disproportionation into silicon occurs. The apparatus consists of 2 identical polymer trapping vessels directly adjacent to a region capable of being heated to 850°C , Figure 1a and 1b. These two units are connected

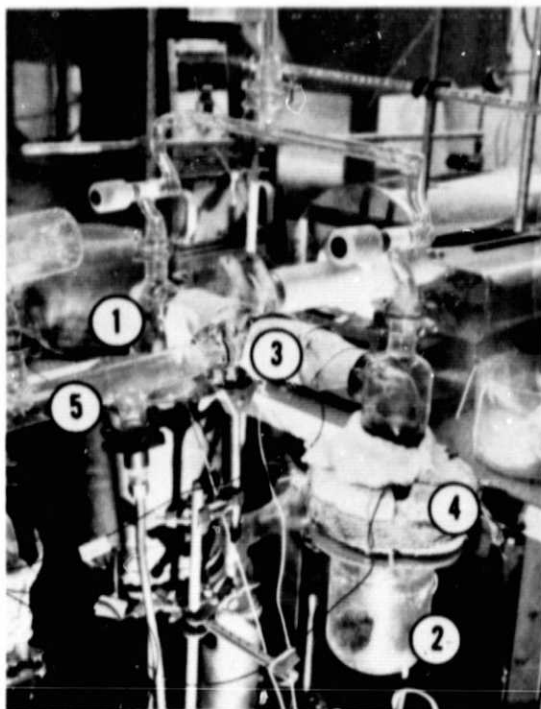
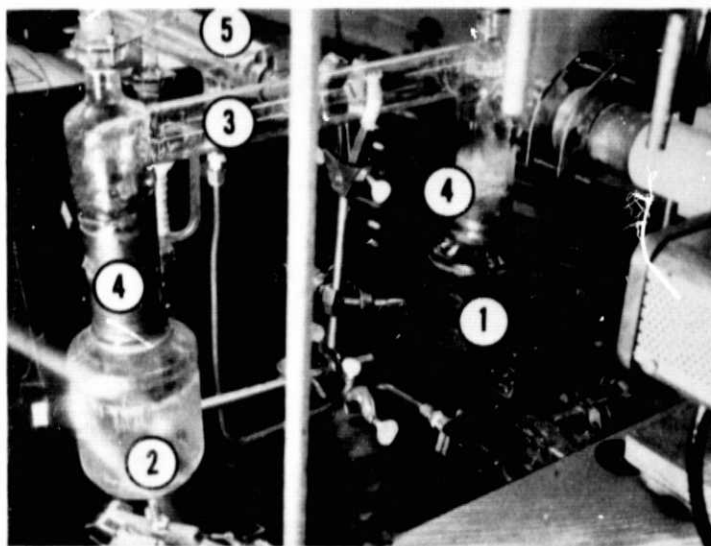


Figure 1a. Homologue Residue Conversion Unit.

1. Polymer trap 1
2. Polymer trap 2
3. Homologue transport region
4. Hot collar region
5. Mass spectrometer inlet.

Figure 1b. Homologue Residue Conversion Unit.

1. Polymer trap 1
2. Polymer trap 2
3. Homologue transport region
4. Hot collar region
5. Mass spectrometer inlet.



by a 16 inch quartz homologue transport tube heated to 220°C. Polymer formation is allowed to occur in one half of the unit and subsequent thermal conversion drives volatiles past a quartz surface heated to 850°C. Thermal disproportionation of Si_xF_y homologues into silicon occurs in the 850°C zone while the unconverted 20% - 40% are transported across the 220°C zone into the 2nd condensation unit. Subsequent thermal conversion of the residue polymer, $(\text{SiF}_2)_x$, formed from condensed unconverted Si_xF_y homologues drives them past a 2nd 850°C quartz surface affecting disproportionation into silicon and SiF_4 .

In these experiments SiF_4 was passed across a 15 inch zone of mg silicon heated at 1350°C at a flow of 0.24 gms SiF_4 per minute. Formation of polymer from SiF_2 took place (trap 1,) at -78°C in a isopropyl-dry ice slush bath, unreacted SiF_4 was collected. Subsequent to polymer formation, the slush bath was replaced with a heating mantle, and a high resistance furnace heating element was wrapped around the 4" long constriction adjacent to the polymerization trap and connected to a 140 V/10A Variac transformer. This hot collar region was heated to 850°C before power was applied to the heating mantle surrounding the condensation trap. The temperature of the condensation trap was raised to 400°C at a heating rate of 10°C/minute with disproportionation of the oils into silicon in the hot zone occurring over temperature range 200°C to 400°C. An identical procedure is followed to effect thermal disproportionation of the residual polymer $(\text{SiF}_2)_x$ formed from unconverted homologues. High efficiencies of residue $(\text{SiF}_2)_x$ disproportionation into silicon have been realized on this apparatus.

Under these reaction conditions no evidence was observed of oil formation from condensed volatiles in the horizontal homologue transport region. This apparatus and reaction technique has been used to obtain mass spectral data correlating species liberated during thermal conversion with pressure and temperature. Further, data from this apparatus has been collected leading to calculations of % SiF_4 conversion (reaction between SiF_4 and mg Si), % homologue conversion, overall silicon to silicon yield, and residue

$(\text{SiF}_2)_x$ polymer conversion efficiencies.

B. Thermal Disproportionation

Effort is being directed toward studying the parameters affecting homologue conversion on a 500°C to 850°C disproportionation bed packed with Si chunks. The apparatus consists of a polymer condensation trap (Figure 2) feeding a 20 inch quartz tube packed with 1-2 cm silicon chunks. Polymer is formed from SiF_2 in the condensation trap at -78°C from SiF_2 generated at 1350°C from mg Si and SiF_4 . A movable ring heater which craverses the condensation trap at a uniform rate has been constructed and tested (Figure 2). This ring heater allows a relatively constant concentration of homologues to reach the hot bed throughout the course of the experiment.

C. Thermal Stability of $(\text{SiF}_2)_n$

The underlying mechanism of homologue formation from polymeric $(\text{SiF}_2)_n$ and the pyrolysis of this mixture has continued to be of interest. A better understanding of the effect of heat on the polymer would have direct relevance on optimizing conditions for polymer breakdown and homologue transportability. This information would aid in both pilot plant design and the selection of a silicon harvesting technique.

The recycle capability of unconverted polymer has been a prime topic for study during the last quarter, this was included in the thermo-analytical work. An outline of instrumental methods which will be used is given below, together with some preliminary results obtained during this reporting period.

Thermogravimetric Analysis (TGA)

TGA is the measurement of change in weight as a function of temperature (or as a function of time at a fixed temperature). The heart of the instrumental method is an electromagnetic balance to which power is sent to restore the balance to equilibrium when a photosensitive null detector picks up a change in weight in the sample boat. The heating rate and temperature range are

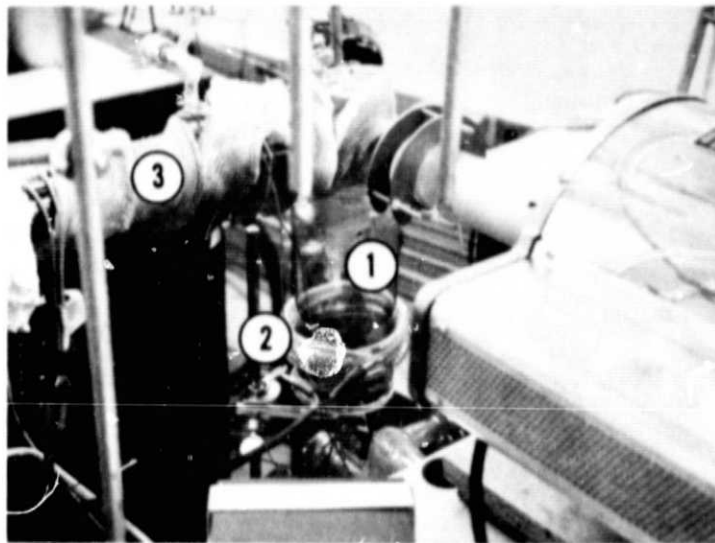


Figure 2. Traversing Polymer Heater

1. Polymer trap
2. Traversing polymer heater
3. Transport tube, hot packed bed.

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accurately controlled by the furnace. The power requirement of the electromagnetic balance is directly proportional to the weight change of the material in the sample boat. TGA is invaluable for studying the thermal behavior of polymers; because the balance pan is enclosed, pyrolysis under different atmospheres is possible. See Figure 3.

We have observed that silicon yields were in the range of 60 — 80% during conversion of the polymer in the hot collar experiments. The unconverted material which collected in the SiF_4 trap appeared to be unchanged polymer. To establish the recycle capability of this material we compared TGA traces of this polymeric residue to the initial polymer. This was done by heating under both vacuum (5×10^{-4} torr) and under one atmosphere of flowing (40 mil/min) argon.

Mass Spectroscopy

The mass spectrum of materials evolved from heating (to 300°C) the initial polymer and the unconverted residue under vacuum have been discussed previously.⁴ At this temperature the differences between mass spectra is considered to be insignificant.

Earlier work, given in Technical Progress Report No. 17, indicated the variation of total ion current and pressure as a function of polymer temperature during conversion. These results illustrate thermal stability hence will be included in the discussion on thermal breakdown.

Differential Scanning Calorimetry (DSC)

DSC is an instrumental method which is capable of measuring quantitatively the enthalpic change from a differential couple as the material under study and a reference sample are programmed over a desired temperature range. A component diagram is shown in Figure 4. One thermocouple has contact with the reference material which should have no change in heat capacity over the temperature range that is to be studied. The sample, which

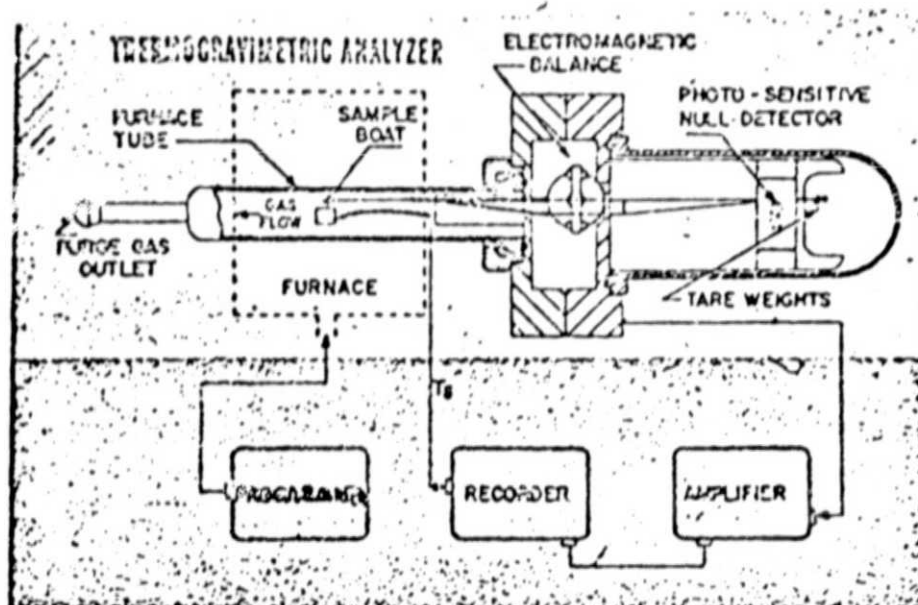


Figure 3. Thermogravimetric Analyzer

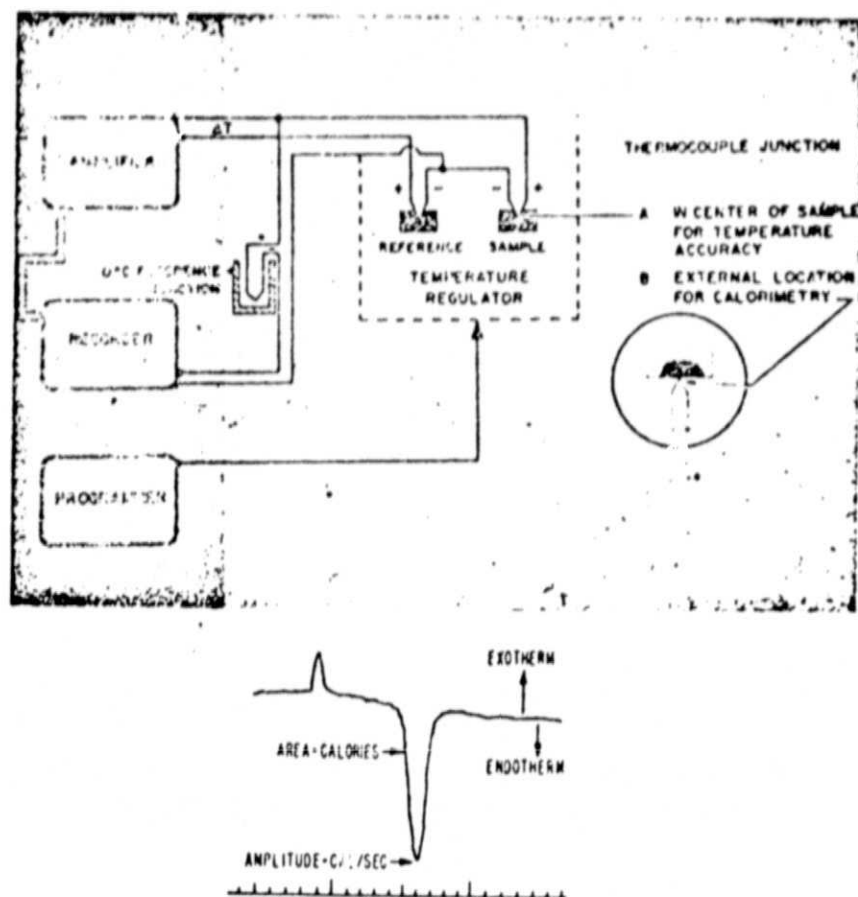


Figure 4. DSC Instrumentation and Typical Trace

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is expected to have a heat change in the temperature range, is contained in a metal can. Although the thermocouple contacts the can (not the sample), provided the heating rate is slow enough, highly accurate transition temperatures can be recorded. The typical chart record shown on Figure 4 has temperature as the abscissa and the ordinate is differential power.

Any transition which involves the absorption or liberation of heat is amenable to study. Of particular interest to the Motorola low-cost silicon program would be (1) a knowledge of the effect of heating rate on polymer/homologue mixtures, (2) determination of transition temperatures during heating (melting and rearrangement would be endothermic, silicon conversion would be exothermic), (3) quantitative ΔH measurements on the reactions and rearrangements which occur. Specific heat can also be measured.

The critical considerations are calibration, small sample size, proper sample encapsulation, and scanning rate. For reproducible work all variables have to be carefully optimized. Generally sample holders are aluminum pans with crimped-on aluminum tops. To eliminate complications from alloys with silicon we decided to use gold pans. During preliminary optimization work the sample size was initially 30 mg; however, this had to be reduced to the range 1-5 mg because rupture of the pan and subsequent leakage of volatile materials induced thermocouple corrosion. For this reason we have not yet optimized the operating conditions for reproducible DSC thermograms. Despite this limitation the preliminary result is of sufficient interest to be included in the discussion.

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR has emerged in recent years as a very powerful tool for the elucidation of chemical structure. This technique is applicable to all nuclei with a magnetic spin, for this reason, it is especially useful to fluorine chemistry where chemical shifts and coupling constants of ^{19}F nuclei are generally larger than those observed in proton NMR spectroscopy.

Assuming the structure $\text{SiF}_3 - (\text{SiF}_2)_n - \text{SiF}_3$, then the ^{19}F NMR spectrum will distinguish between the SiF_3 and SiF_2 groups because they are in magnetically different environments. The fluorine atoms within the groups will absorb radio frequency radiation at different energies giving rise to two separate peaks in an NMR spectrum of different relative area and fine structure. By comparing peak areas the value of n (hence molecular weight) can be calculated. With this objective in mind, a sample of the homologues was sent to Kenneth Sharp at USC. For this work solid polymer cannot be examined, samples have to be in the liquid state.

D. Capture of SiF_2 and Homologue Liberation

For pilot plant design considerations, the condensation of polymer and subsequent liberation of homologues is of considerable interest. Previous technical reports have suggested utilizing a bed of silicon granules as the condensed substrate. This would have the advantage of being used as the substrate for conversion, hence minimizing losses due to inefficient transfer from the condenser to the harvester (converter). For this reason the initial work focused on a silicon condenser bed to determine the efficiency of condensation and liberation.

The apparatus (Figure 5) consists of a silicon bed (chunks, 0.25" $\rightarrow$ 0.75") housed in a pyrex jacket through which acetone coolant was circulated. The acetone was cooled by passing it through a copper heat exchanger coil partially immersed in dry ice/acetone. Taps T_1 and T_2 were incorporated in the system. By sealing the condenser unit at either end this allowed the direct weighing of the unit, hence the weight increase attributable to polymer condensation. The temperature of the bed was measured by inserting a thermocouple into the well (w) which was aligned to be coincident with the center of the bed.

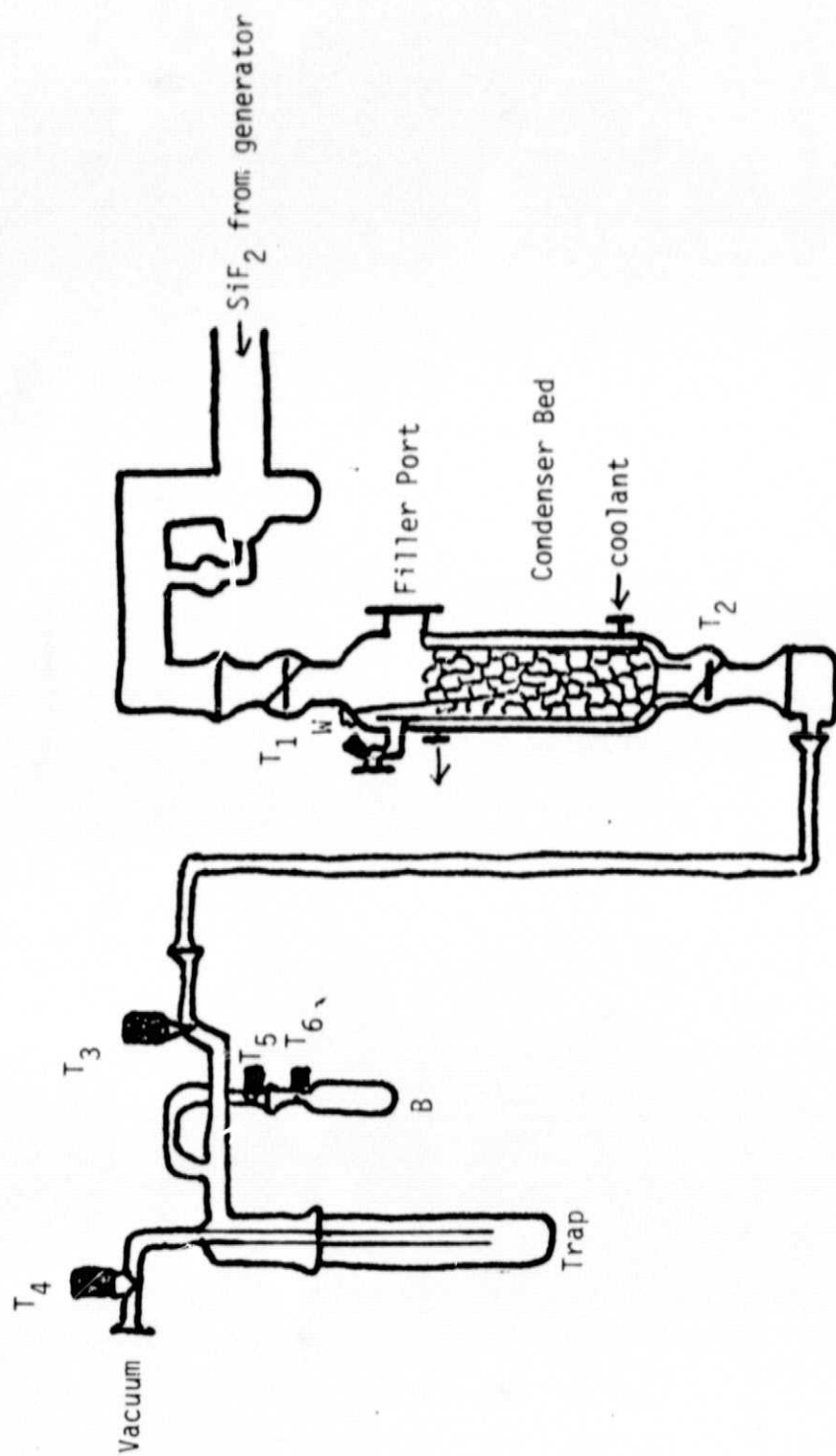


FIGURE 5.
Diagram of SiF_2 capture and homologue liberation apparatus.

SiF_2 , generated by passing SiF_4 over a silicon bed at $1350 \pm 30^\circ\text{C}$, was passed through the system at a known (pre-calibrated) flow rate. After passage of 100-150 gms of SiF_4 , taps T_1 , T_2 , T_3 and T_4 were closed and the amount of unchanged SiF_4 determined by transferring from the trap to the pre-weighed sample bottle (B). The amount of polymer trapped in the condenser bed was determined by disassembling the system and reweighing the condenser bed.

E. Modifications Made on the Near-Continuous Silicon Purification Apparatus

Modifications were made to the near-continuous silicon purification apparatus to facilitate longer run times, better temperature and pressure monitoring and particulate removal.

i) Replacement of the solenoid actuated all quartz ball and socket valves with a manually operated quartz ball valve sealed by a teflon to quartz seal.

ii) A fixed polysilicon bed employing loosely packed chunks of sg silicon. The bed will facilitate silicon harvest from the near-continuous reactor. Silicon will be deposited onto the bed via C.V.D. of the Si_xF_y homologues at $\sim 850^\circ\text{C}$.

iii) Reinstatement of a baffle design similar to one employed earlier.

iv) The addition of electronic solenoid actuated pressure transducers for multiple pressure measurements.

v) An additional low temperature coil was incorporated for trapping unconverted Si_xF_y homologues. The Si_xF_y homologues which could pass through the 850°C packed bed will stop on the low temperature coil. The coil offers a high volume means for trapping the unconverted homologues.

vi) Additional temperature controllers for more accurate monitoring and maintaining temperatures of the $(\text{SiF}_2)_x$ conversion at a specific temperature or during incremental temperature increases. The temperature at which the $(\text{SiF}_2)_x$ converts into the Si_xF_y homologues needs to be scrutinized.

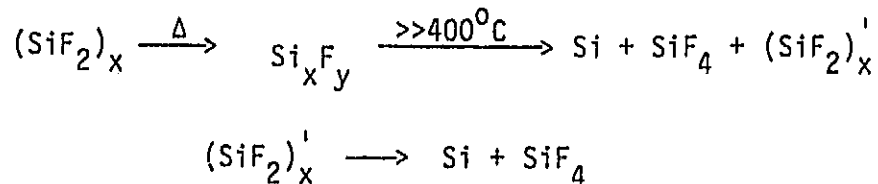
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III RESULTS AND DISCUSSION

A. Chemical Analysis of Homologues

It is within the scope of this study to more clearly define the properties and chemistry of the Si_xF_y homologues so that disproportionation of the volatile products liberated during thermal conversion of the $(\text{SiF}_2)_x$ polymer can be optimized.

Analysis of data correlating pressure changes occurring during polymer conversion with conversion temperature and homologue composition as measured by mass spectrometry has been presented.⁴ Data with regard to homologue conversion efficiency has indicated that under non-optimized reaction conditions, polymer conversion efficiencies of from 60% to 80% can be reproducibly achieved. Further, it has been observed that following thermal conversion, the unconverted volatile fraction (20% to 40%) reforms as a polymer-like material at liquid N_2 temperatures.



While it should be noted that optimization of the thermal disproportionation reaction apparatus would reduce the remaining unconverted fraction, $(\text{SiF}_2)_x'$, to a few percent, a series of experiments has been undertaken to study the chemistry of both the $(\text{SiF}_2)_x$ and volatile products liberated from these during thermal conversion and also the polymer formed $((\text{SiF}_2)_x')$ from condensed homologues liberated during $(\text{SiF}_2)_x$ conversion. The chemistry studies have focused on mass spectrometry of the volatile homologues liberated from $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$ thermal gravimetric analysis (TGA) comparison of $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$, and differential scanning calorimetry (DSC) analysis of $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$.

Table I presents data regarding the gas phase composition of homologues liberated during conversion of $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$. Here it will

TABLE 1

Si_xF_y MASS SPECTRAL DATA COMPARISON

MASS NUMBER	ASSIGNMENT		ORIGINAL POLYMER	(SiF ₂) _n '
	x	y		
47	1	1		
66	1	2		
85	1	3		
113	2	3		
132	2	4		
151	2	5		
167	Si ₂ O ₂ F ₅			NO
195	Si ₃ O ₂ F ₅			NO
198	3	6		
222	3	2		
236	3	8		
264	4	8		
283	4	9		
292	5	8		
302	4	10		
311	5	9		
330	5	10		
349	5	11		
377	6	11		
396	6	12		
415	6	13		
462	7	14		
481	7	15		
528	8	16		
547	8	17		
575	9	17		
594	9	18		
660	10	20		
726	11	22		

Except where stated (No), all ions of the above mass numbers were observed.

be noted that both the original polymer and the residue polymer formed from volatiles liberated during the thermal conversion of $(\text{SiF}_2)_x$ liberated a series of homologues of similar composition. However, the small concentration of oxygen containing species liberated from $(\text{SiF}_2)_x$ were not observed during the thermal conversion of the residue polymer $(\text{SiF}_2)_x$. The relative intensities of the major species liberated during thermal conversion of $(\text{SiF}_2)_x$ have been previously reported.⁴ However, due to the very low intensity of the peaks above $m/e \sim 200$ with respect to $m/e 85$, integration of homologues presented in Table I was not undertaken. The mass spectral data clearly indicates that $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$ undergo thermal conversion in a similar manner and liberate essentially the same series of volatile homologous silicon fluoride compounds.

B. Homologue Conversion Experiments

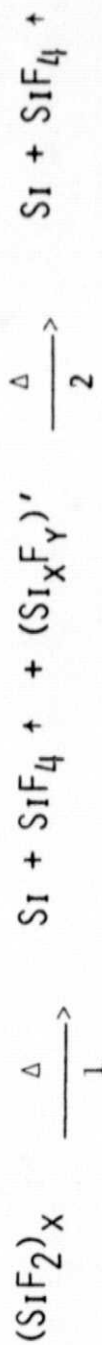
Data correlating homologue efficiency with residence time of Si_xF_y species in a non-optimized thermal conversion unit has shown that conversion efficiencies of 60% to 80% can be achieved. A series of experiments has been undertaken to study the thermal disproportionation of the polymer $(\text{SiF}_2)_x'$ formed from condensed volatiles liberated during the conversion of $(\text{SiF}_2)_x$. In this series of experiments a double polymer condensation-polymer disproportionation unit has been utilized. This apparatus consists of two quartz polymer trapping vessels in close proximity (2 inches) to a region capable of being heated to 850°C (Figures 1a and 1b). In this apparatus residue polymer 20% to 40% of total polymer weight formed from unconverted $\text{Si}_n\text{F}_{2n+2}$ homologues has been shown to undergo thermal disproportionation into silicon with conversion efficiencies consistent with earlier homologue conversion experiments.⁴

Table II presents data leading to an overall polymer conversion efficiency calculation. Here, from weights of SiF_4 liberated and weights of polymer formed and converted the efficiencies of the conversion of $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$ into silicon can be obtained. It will be noted that the conversion efficiency for stage 1 is 77%, this correlates extremely well with

TABLE II

RESIDUE $(Si_xF_y)'$ CONVERSION BASED ON INDIVIDUAL STAGE CALCULATION

No. 1



STAGE 1 - CONVERSION

GMS POLYMER
FORMED
14.13 g.GMS POLYMER
CONVERTED
10.81 g.GMS RESIDUE
FORMED
3.32 g.%CONVERSION
STAGE 1
77%

STAGE 2 - CONVERSION

GMS RESIDUE FORMED
3.32 g.GMS RESIDUE
CONVERTED
3.02%CONVERSION
91%OVERALL POLYMER
CONVERSION

$$\text{OVERALL CONVERSION} = 0.77 + (0.91 \times 0.23) = 98\%$$

previously reported data.⁴ Furthermore, a 91% conversion efficiency for the residue $(\text{SiF}_2)_x$ polymer has been achieved. Due to the fact that conversion efficiency has been observed to be inversely proportional to residence time, this high conversion efficiency is consistent with previously reported results⁴ showing a direct relationship between residence time and conversion efficiency of $(\text{SiF}_2)_x$ polymer into silicon.

Table III presents data showing conversion efficiencies of polymer into silicon for two experiments using the double condensation/disproportionation unit to convert both $(\text{SiF}_2)_x$ and $(\text{SiF}_2)_x'$ into silicon. Here it will be noted that an overall mean polymer conversion efficiency of 95.7% has been achieved!

C. Thermal Disproportionation on Packed Beds

In order to study the parameters affecting conversion efficiencies on a hot Si bed, elimination of variables concerning the rate of liberation of volatile homologues from the polymer trap is required. Therefore, the first step in the packed bed studies has been to develop and install a polymer trap heating system capable of liberating homologues at a constant rate throughout the course of the reaction. The ring heater which traverses the condensation trap has been demonstrated to achieve this initial goal. The preliminary packed bed work has been designed to define approximately the various factors affecting the conversion, make necessary design modifications and incorporate these facts into a cohesive experimental plan. Future work will focus on effect of bed temperature, particle size, bed length and polymer liberation rate on overall silicon to silicon conversion efficiencies.

D. Polymer Analysis by TGA, DSC, and NMR

Because of the pyrophoric character of the polymer the TGA electromagnetic balance unit was housed in an argon-purged glove box. Several

TABLE III

RESIDUE (Si_xF_y)' CONVERSION BASED ON POLYMER INPUT / OUTPUT

NO.	1	2
	14.1 G.	15.4 G.
	13.8 G.	14.9
	98%	97%
		97.5%

experiments were run until reproducible thermograms were obtained. Difficulties in attaining reproducibility were thought to be due to the inherent moisture sensitivity of the polymer.

Figure 6 compares the difference in thermal behavior of the initial polymer heated under vacuum and under one atmosphere of flowing argon. Apparently the material undergoes a significant weight change in the region $280^{\circ} - 300^{\circ}\text{C}$. The shape of the thermogram suggests that the majority of weight loss occurs over a narrow range. At 280°C the polymer has undoubtedly converted to homologues. Mixtures would exhibit a boiling range. Hence, the weight change is probably due to a chemical reaction common to all components. Volatilization of low molecular weight material is the cause of the initial (to $\sim 250^{\circ}\text{C}$) weight loss. The species evolved were probably contained in the polymer. As expected, a vacuum atmosphere accelerates this initial weight loss.

All experiments involving homologue transport and harvesting have been performed under vacuum. Compared to one atmosphere of argon the effect of vacuum is to move the near-vertical weight loss region to lower temperatures. This is due to more rapid removal of volatile reaction products.

TGA can be used to obtain semiquantative data, for example, inorganic filler % in plastics. Volatile evolution precludes such measurements from thermograms of $(\text{SiF}_2)_n$. However, at pressures higher than atmospheric, volatile loss could be reduced to a level where reasonable stoichiometric correlations with theoretical silicon yield could be observed.

This data confirms the previously reported mass spectroscopy and pressure variation work.⁴ The total ion current and pressure exhibit maxima at $\sim 290^{\circ}\text{C}$. A second peak appeared at 400°C ; under the experimental conditions chosen for TGA runs the second peak is observable but less significant.

Figure 7 compares behavior under vacuum of initial polymer and the

SAMPLE: Figure 6
Effect of Heat in
Argon - (A)
Vacuum - (B)
on Initial Polymer

SIZE mg.

X-AXIS

TEMP. SCALE 100 °C
inch

SHIFT 0 inch

Y-AXIS

SCALE 5 mg.
inch
(SCALE SETTING X 2)

SUPPRESSION

mg.

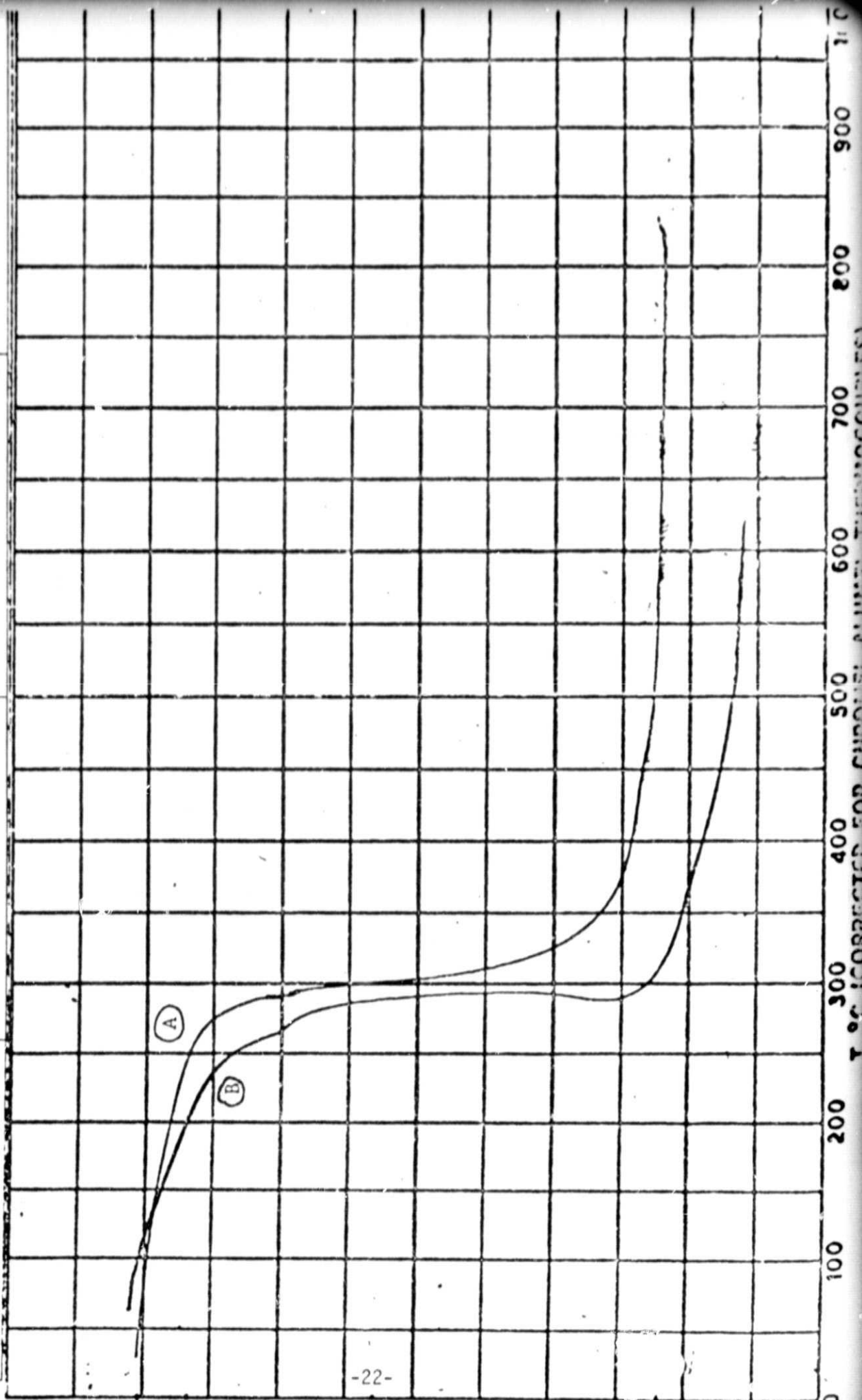
RUN NO.

OPERATOR CT

HEATING RATE 10°C
min.

ATM. Argon / Vacuum

TIME CONSTANT 1 sec.



SAMPLE: Figure 7

Comparison of Initial
Polymer - (A)

Polymeric Residue (B)
Heated Under Vacuum

SIZE mg.

X-AXIS

TEMP. SCALE 100 $^{\circ}\text{C}$ inch

SHIFT 0 inch

Y-AXIS

SCALE 5 (A) mg.
10 (B) inch
(SCALE SETTING X 2)

SUPPRESSION mg.

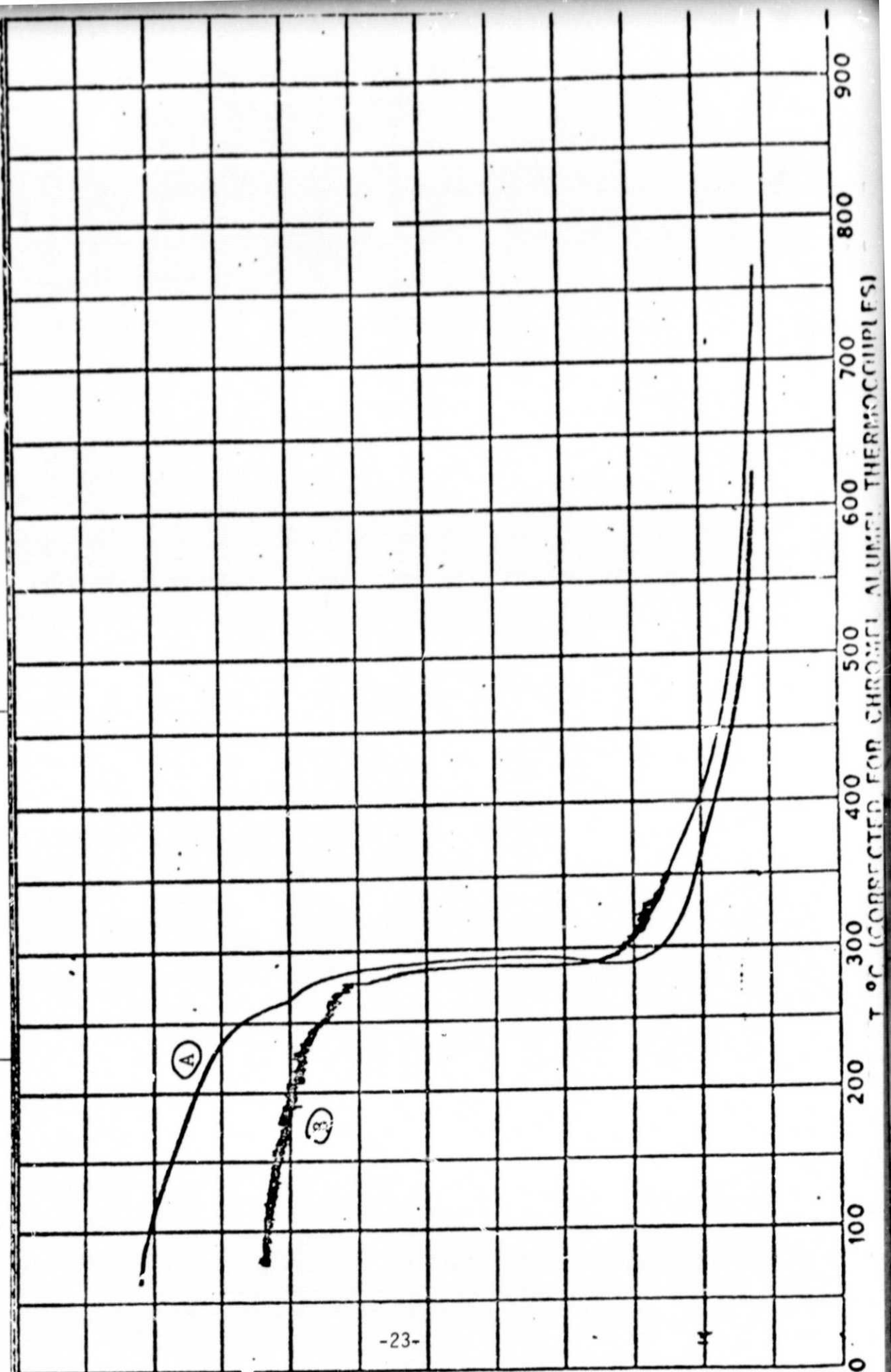
RUN NO. DATE

OPERATOR CT

HEATING RATE 10 $^{\circ}\text{C}$ min.

ATM. Vacuum

TIME CONSTANT 1 sec.



WEIGHT, mg.

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polymeric residue. The lack of coincidence is due to different weights in the sample boat. The overall shape is very similar, decomposition temperature differing by only $\sim 10^{\circ}\text{C}$.

Figure 8 compares thermal stability in argon. The polymeric residue appears to contain material of higher thermal stability than the parent polymer, although the difference is less significant when pyrolyzed under vacuum. Reasons for this behavior are not immediately apparent.

The DSC curve exhibited a rapid sharp exotherm occurring at 330°C followed immediately by a broad endothermic transition which persists to 390°C . Although it is not valid to quantify on the basis of this preliminary result, we can conclude that the overall heat taken in is significantly larger than the exothermic heat. This is in agreement with an endothermic trend observed occasionally during TGA measurements; for example curve B of Figure 6 drifts towards the y axis during the decomposition period. Further work will be necessary to correlate DSC and TGA results.

The NMR spectrum was surprisingly complex. At USC the mixture had to be distilled to remove solid materials. ^{19}F spectra run on the undistilled mixture and the distillate were very similar. Four groups of peaks; two minor peaks at 109 ppm (F-Si-O), 139 ppm ($\text{Si-SiF}_2\text{-Si}$), a larger peak at 155 ppm (possibly -SiF_3) and a large complex centered at 172 ppm (all relative to CFCl_3). The appearance of the signal at 172 ppm can only be explained by the presence of highly shielded fluorine atoms, for example fluorine attached to a cyclic silicon structure. This peak had a relatively larger contribution in the spectrum of the undistilled mixture.

The exact thermal history of the samples is not known, distillation at USC may have changed the composition and structure of the components. This work may be pursued in conjunction with a University possessing the appropriate instrumentation. Alternatively, an in-house spectrometer may be acquired by Motorola for similar analysis involving organic structures.

SAMPLE: Figure 8

Comparison of Initial
Polymer - (B)
Polymeric Residue - (A)
Heated Under Argon

SIZE mg.

X-AXIS

TEMP. SCALE 100 °C
inch

SHIFT 0 inch

Y-AXIS

SCALE 5 mg.
inch
(SCALE SETTING X 2)

SUPPRESSION mg.

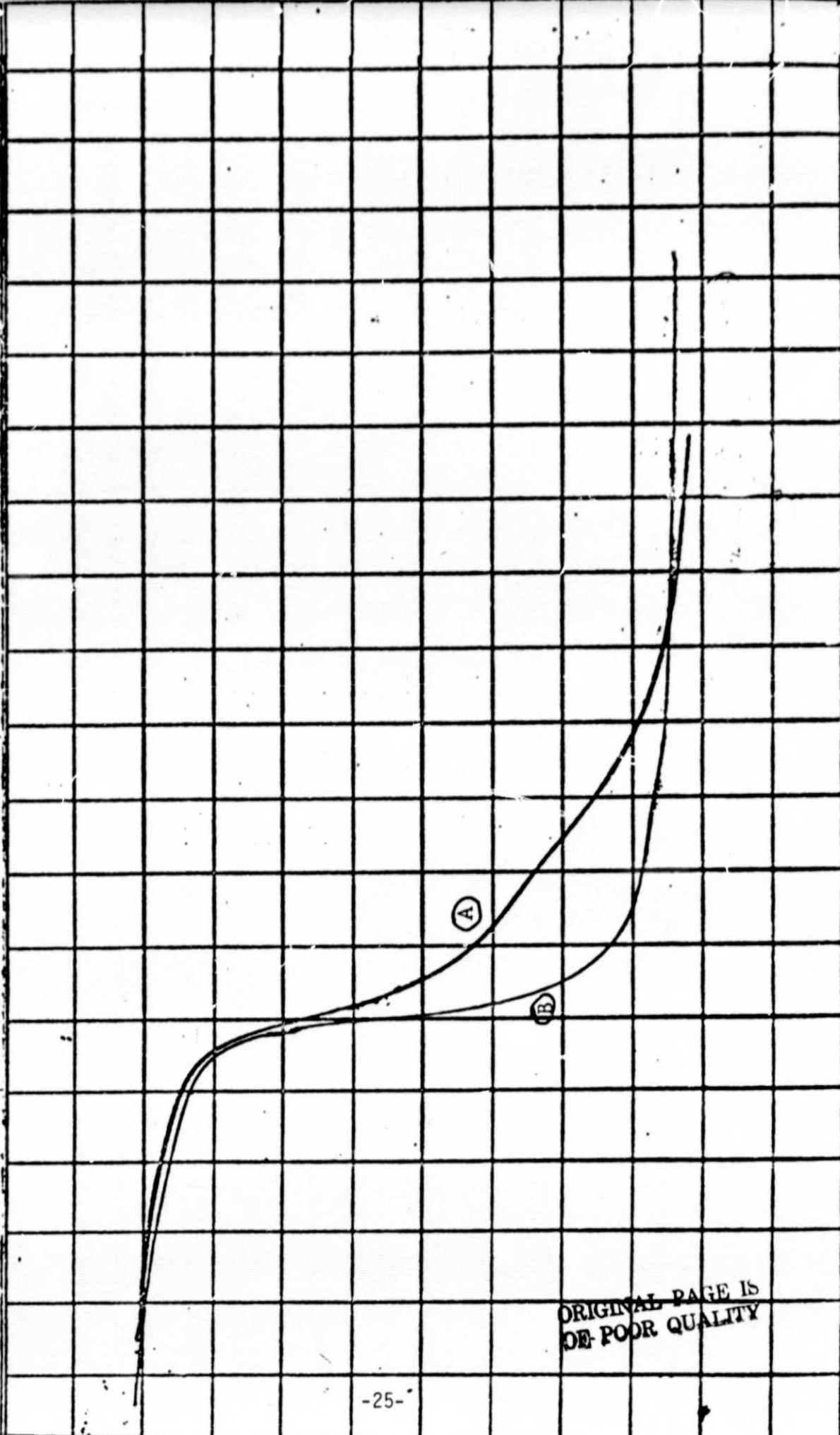
RUN NO. DATE

OPERATOR CT

HEATING RATE 10 °C
min.

ATM. Argon

TIME CONSTANT 1 sec.



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T °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

E. $(\text{SiF}_2)_x$ Polymer Transport on the Near-Continuous Purification Apparatus

Two series of experiments were conducted during the past quarter for optimization and feasibility demonstration of the Near-Continuous Purification Apparatus. In general, two runs on the apparatus were conducted each day.

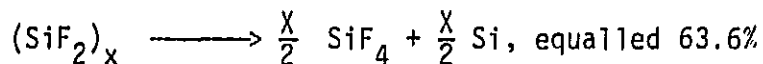
Specifically the results from the first series of experiments can be found in Table IV. Each run in this series lasted for 30 minutes except #4 which was terminated early because of low SiF_4 inlet pressure. Run 1 was a flow meter calibration experiment where no polymer was made and run 5 is a recycle experiment.

In this series the following observations were made:

- (a) Average efficiency of step 1, i.e.,



- (b) Average efficiency of step 3, i.e.,



- (c) Recycle efficiency equalled 66%.

- (d) The average silicon transport rate over the two hours equalled 27.36 gm/hr with an overall polymer to silicon efficiency (one recycle included) of 87.9%

In the second series of experiments longer runs were achieved at the same silicon transport rate. In this series, runs A and B, (see Table V) represent calibration runs and run 8 was used to recycle the unconverted homologues through the 850°C hot zone and bake the system. The flow meter was calibrated at 100 ± 2 gms SiF_4 (per 30 minutes). Thus runs 1 and 2 represent 30 minute runs; 3-5 equal 60 minute runs; and 6 and 7 equal 120 minute runs. An overall silicon transport rate of 24.9 grams silicon purified per hour during the total eight hours of run time was observed.

To further characterize the process, a silicon mass balance was conducted during the second series of experiments. The grams of mg Silicon reacted was obtained by weighing the mg Silicon charge before the first

TABLE IV.

Series 1. NEAR CONTINUOUS TRANSPORT.

RUN* #	SiF ₄ Deliv.	SiF ₄ Unrx.	SiF ₄ from Conv.	Silicon Tran.	SiF ₄ Remain.	Si to Si (%)
1	96 gm	SiF ₄ delivered in 30 minute calibration run.				
2	96.0	35.1 gm	48.1 gm	12.95 gm	12.3 gm	79.8%
3	96.0	35.9	37.8	10.18	22.3	62.9
4	80.0	29.6	12.0	3.23	38.4	25.3
5	96.0	45.9	43.3	11.66	6.8	86.4
6	RECYCLE	----	53.6	14.43	---	67.2%
AVG. 63.6%						
TOTALS	368 gm	146.5 m	194.8 gm	52.45 gm	26.7	87.9%

* All runs were for 30 minutes duration except for #4 which was only for 25 minutes.

Si Transport rate equaled 27.36 gm/hr.

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TABLE V.

SERIES 2. NEAR CONTINUOUS TRANSPORT

RUN #	SiF ₄ DELIVERED (GM)	SiF ₄ UN RX (GM)	% SiF ₄ RXN (1/2)	SI RXN (GM)	SiF ₄ OUT (GM)	Si* OUT (GM)	SI TO SI (1/2)
(A)	102.7						
(B)	36.1						
1.	100	33.2	68.8	18.0	16.9	4.6	25.6
2.	100	29.0	71.0	19.1	16.7	4.5	23.6
3.	200	58.6	70.7	38.1	45.5	12.3	32.3
4.	200	58.3	70.9	38.2	89.8	24.2	63.4
5.	200	67.7	66.1	35.6	64.5	17.4	48.9
6.	400	130.9	67.3	72.5	157.2	42.3	58.3
7.	400	191.4	52.2	56.2	95.6	25.7	45.7
8.	RECYCLE AND BAKE				172.8	46.6	
TOTAL	1600GM	569.2		277.7	65.90	177.6	64%

(198.6 WEIGHED)**

* SAMPLES SENT FOR ANALYSIS.

** THIS REPRESENTS AN OVERALL TRANSPORT RATE OF 24.9 GM/HR.

run and after the eighth run. The 1107 gms charge was observed to lose 364 gms. The silicon purified weighed 199 gms. In addition, impure silicon obtained from thermally decomposing the prepolymer in the baffle weighted 167 gms.

Therefore Silicon in = 364 ($\pm$ 5 gm) gms.

Silicon out = 199
 $+ 167$

 366 ($\pm$ 5 gm)gms.

The observed Silicon transport rate equalled $\frac{198.9}{8 \text{ hours}}$ gm/ = 24.9 gm/hr.

F. Capture of SiF₂ and Homologue Liberation Experiments.

The initial phases of the investigation of polymer condensation and subsequent liberation will be directed at determining the efficiency of stationary silicon beds. Alternate condenser configurations are being designed with later work possibly to center on quartz coils.

The condenser was charged with silicon chunks (1.669 Kg), SiF₄ fed into the reactor and unreacted SiF₄ collected in the trap. The results from two preliminary runs are given below; yield and polymer is calculated from the theoretically obtainable amount after subtracting the weight of unreacted SiF₄.

Bed Temperature	Run 1	Run 2
	29($\pm$ 2) ^o C	-30($\pm$ 2) ^o C
Wt of polymer formed	= 123.1 g	48.7 g
Polymer trapped in condenser	= 36.3 g	42.3 g
Polymer recovered from SiF ₄ trap	43.6 g	2.0 g
Bed efficiency	= 29.5 %	86.8 %
Polymer lost in system	= 43.2 g	4.4 g

Polymer recovered from the SiF₄ trap was determined by weighing the trap after transfer of all SiF₄ to the adjacent weighing bulb. Most of the

polymer lost in the system appeared to collect in a glass wool trap located immediately below the condenser unit. On opening the system this material burned, hence it was not possible to get an exact weight.

These preliminary runs suggest that silicon bed temperature has a significant effect on collection efficiency. Lowering the temperature by 60°C increases the percentage polymer captured considerably. Other significant variables, such as packing density of the silicon bed, length and flow rate will be investigated after the effect of temperature has been fully investigated.

G. Economic Analysis

A further look at the process economics with recycle of the Si_xF_y unconverted polymer was made as shown in the process flow diagram of Figure 9. Note that 1.19 Kg Si is produced and only 0.29 Kg SiF_4 makeup is needed compared respectively to 1.00 Kg Si and 0.61 Kg SiF_4 without Si_xF_y recycle. The same assumptions as Quarterly Report No. 7 are used with the additional assumption of a 5% loss of Si product.

The production costs for a \$10 million fixed capital investment are summarized in Table VI, based on 1.00 Kg Si produced. It gives a total product cost of \$7.68 compared to \$8.96 without Si_xF_y recycle.

The product cost as a function of fixed capital investment and SiF_4 cost is shown in Figure 10 with solid lines for no recycle and the dashed line for Si_xF_y recycle. Since less than half the SiF_4 makeup is used in the recycle case, the sensitivity to SiF_4 cost is also less than half the non-recycle case. Thus, the recycle of Si_xF_y allows the total product cost to be below \$10/Kg Si for up to \$16 million fixed capital investment.

ESTIMATION OF TOTAL PRODUCT COST WITH $Si_x F_y$ RECYCLE

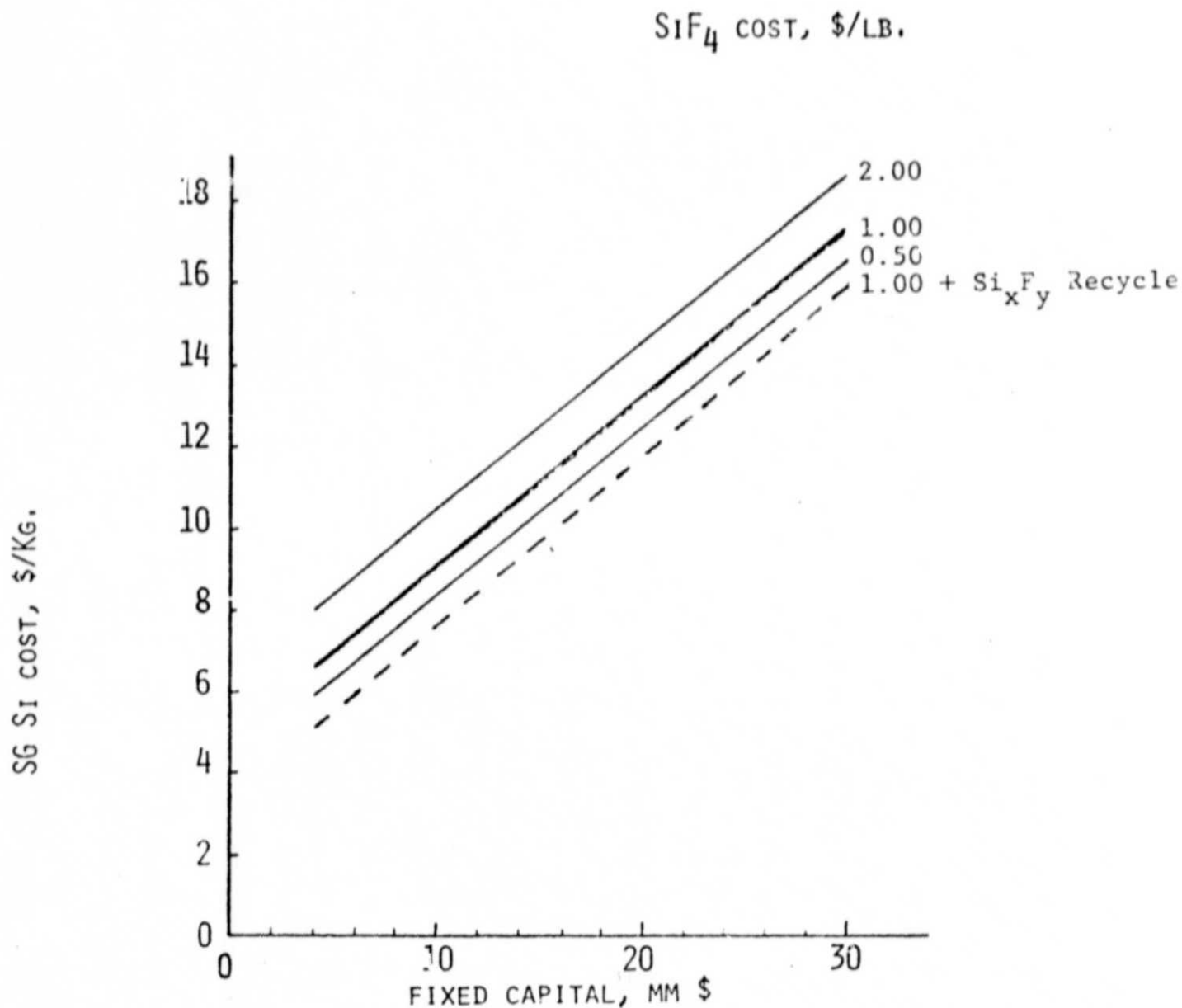
(\$ PER KG SG SI PRODUCED)

1. DIRECT MANUFACTURING

1. RAW MTLs, MG SI	1.11 KG X \$1.00/KG	1.11
SiF_4	0.24 KG X \$1.00/LB X 2.2 LB/KG	0.54
2. DIRECT OP. LABOR 10 MEN/SHIFT	$\frac{5}{5}$ SKILLED @ 6.90/HR X .0372 = .26 $\frac{5}{5}$ SEMI-SK @ 4.90/HR X .0372 = .18	0.44
3. UTILITIES ELECTRICITY	7.4 KW-HR X \$.03/KW-HR	0.22
	REFRIGERANT 0.0161 MM BTU X \$20/MM BTU	0.32
4. SUPERVISION/CLERICAL	15% OF 1.2	0.07
5. MAINT. & REPAIRS	10% OF FIXED CAPITAL (\$10 MM)	1.00
6. OPERATING SUPPLIES	20% OF 1.5	0.20
7. LABORATORY CHARGE	15% OF 1.2	0.07

2. INDIRECT MANUFACTURING

1. DEPREC./LOCAL TAXES/INSURANCE/INTEREST, 21% OF FIXED CAP.		2.10
(10%) (2%) (1%) (8%)		
3. PLANT OVERHEAD, 60% OF 1.2 + 1.4 + $\frac{1}{2}$ 1.5		0.61
4. TOTAL MANUFACTURING COST		6.68
5. GENERAL EXPENSES, ADMIN/DIST. & SALES/R & D 15% OF MAN. COST		1.00
(6%) (6%) (3%)		
6. TOTAL COST OF PRODUCT		7.68



SG SILICON PRODUCTION COST vs FIXED CAPITAL
INVESTMENT FOR VARIOUS SiF₄ COSTS

FIGURE 10.

IV CONCLUSIONS AND RECOMMENDATIONS

During the past quarter continued experiments further support the following conclusion.

The $\text{Si}_n\text{F}_{2n+2}$ homologues in no way impair the overall efficiency of the $(\text{SiF}_2)_x$ polymer transport purification process. Further support for this conclusion is based upon the following:

1. Spectroscopic analysis comparing the $(\text{SiF}_2)_x$ polymer and the Si_xF_y homologues demonstrate that chemically both materials are essentially identical which explains the nearly identical thermal analysis behavior.
2. Fixed silicon particle beds have been demonstrated to be an effective method for silicon recovery from the Si_xF_y homologues.
3. Transport rates of 25 gms/hr were achieved for repeated 2 hr runs. The silicon mass balance was ~100%.
4. A modified economic analysis incorporating Si_xF_y recycle predicts that silicon from this process should cost \$7.68/Kg to produce at an assumed \$10 MM fixed capital investment.

Therefore it is recommended that the studies be carried out dictated by the program plan/milestone chart, leading to significant conclusions and points of decision within the next quarter's effort.

V NEW TECHNOLOGY

The following new technology items have been uncovered during this reporting period.

I. Description - Bakeable, Double Action, Quartz Ball Valve

Innovators - William M. Ingle
Carl Goetz

Progress Reports - Technical Progress Report No. 18
July 1977

Pages - Report No. 18, Pages 8, 9, and 10

Date Reported - December 9, 1977

II. Description - Purification of Mr Silicon Via Atmosphere Control II

Innovators - William M. Ingle
Stephen W. Thompson
Robert E. Chaney

Progress Reports - Technical Quarterly Report No. 6
July 1977

Pages - Report No. 6 Page 11 - 17 and Appendix I

Date Reported - December 9, 1977

VI PLANS

During the upcoming quarter we plan to continue to operate the near-continuous apparatus for longer run time (≥ 2 hrs.) on a daily basis. This will produce silicon samples for chemical analysis, and electrical characterization.

We will also continue to investigate SiF_2 condensation and silicon harvesting techniques. The best harvesting technique will be identified and experimental studies will be carried out to characterize the important operating parameters on both the small-scale apparatus and the near-continuous apparatus.

We plan to begin the sizing and costing of the equipment for the 1000 metric ton/year plant.

REFERENCES

1. Shafer, Chemical Transport Reactions, Academic Press, 1964.
2. Pease, U.S.A. Patent No. 2,840,588, June 1958.
3. Tims, Kent, Ehlert and Margrave, J. Amer. Chem. Soc., 87,2824 (1965).
4. Ingle, Chaney, Thompson, Technical Quarterly Report No. 6, JPL/ERDA Contract No. 954442, July 1977.